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VARIABLE TEMPERATURE ^{13}C AND ^{29}Si CP/MAS NMR STUDIES OF
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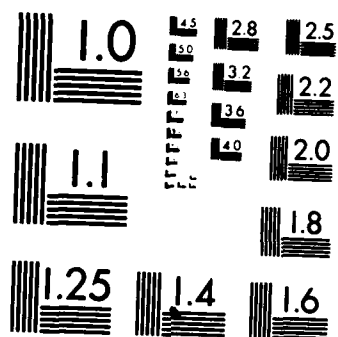
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"VARIABLE TEMPERATURE ^{13}C AND ^{29}Si CPMAS
NMR STUDIES OF POLY(Di-n-Hexylsilane)"

by

G. C. Gobbi, W. W. Flemming, R. Sooriyakumaran, R. D. Miller

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and/or along the silane backbone. A single C-1 resonance is observed at higher temperatures. At temperatures where two silicon resonances are observed, the C-2 and C-3 methylene carbons are each simultaneously observed as broad and narrow resonances. The broad component is dominant at low temperatures which corresponds to the downfield all trans silicon resonance while the narrow component observed at higher temperatures corresponds to the high field silicon resonance. The C-4 through C-6 resonances are observed to be relatively narrow but their motions are not isotropic. We suggest that the silicon backbone is all trans at low temperatures, and that steric constraints lock in the three nearest methylene carbons into a rigid chain while the reduced steric crowding of the outermost carbons permits rapid motions more typical of aliphatic chains. At temperatures about the 305-310K phase transition the silane backbone undergoes fast local motions characterized by a time average conformation, and the hexyl sidechains also experience significantly increased motion. The results are consistent with the hypothesis that the thermochromic UV shift recently observed is due to a transformation of the polymer backbone from an ordered trans conformation to a highly disordered conformation.

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Variable Temperature ^{13}C and ^{29}Si CPMAS NMR Studies of Poly(di n-hexylsilane)

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ABSTRACT: Poly(di n-hexylsilane) has been studied in the solid state using variable temperature ^{13}C and ^{29}Si CPMAS NMR spectroscopy. It has been found that the silane backbone exists in different conformations above and below the thermochromic temperature transition of ca. 307°K. The low temperature form is characterized by a silicon resonance at ca. -20.8ppm which is assigned to the all trans conformation, consistent with other spectroscopic and theoretical calculations. As the temperature was increased above the lowest measured value of 240°K, a second narrow peak at ca. -24.1ppm was observed upfield of the all trans peak in the ^{29}Si NMR spectra. The relative area of the upfield peak increased gradually from 280 to 304°K until about 25% of the intensity was in the upfield resonance. At 310°K a sharp transition occurs, and the remaining 75% of the low field peak completely disappears. The aliphatic side chains at low temperatures are tightly restricted with the C-1 methylenes present in two conformations at temperatures below 300°K. These two C-1 conformations are present in equal populations and are probably rigid and alternating across and/or along the silane backbone. A single C-1 resonance is observed at higher temperatures. At temperatures at which two silicon resonances are observed, the C-2 and C-3 methylene carbons are each simultaneously observed as broad and narrow resonances. The broad component is dominant at low temperatures which corresponds to the downfield all trans silicon resonance while the narrow component observed at higher temperatures corresponds to the high field silicon resonance. The C-4 through C-6 resonances are observed to be relatively narrow but their motions are not isotropic. We suggest that the silicon backbone is all trans at low temperatures, and that steric constraints lock in the three nearest methylene carbons into a rigid chain while the reduced steric crowding of the outermost carbons permits rapid motions more typical of aliphatic chains. At temperatures above the 305-310°K phase transition the silane backbone undergoes fast local motions characterized by a time average conformation, and the hexyl sidechains also experience significantly increased motion. The results are consistent with the hypothesis that the thermochromic UV shift recently observed is due to a transformation of the polymer backbone from an ordered trans conformation to a highly disordered conformation.

Soluble high molecular weight substituted silane polymers are a new class of radiation sensitive materials¹ which have demonstrated ceramic and lithographic applications²⁻⁴. Much of the recent scientific interest in these materials has centered around their unusual electronic spectra^{5,6}. In this regard, substituted silane polymers all show an intense and molecular weight dependent absorption in the UV⁶. Recently, it has been shown that certain polysilanes are also thermochromic both in the solid state⁷ and solution^{8,9}, a property which has tentatively been attributed to the formation of a trans backbone conformation at low temperatures. The present study was undertaken to investigate the dynamic characteristics of poly(di-n-hexylsilane) in the solid state by variable temperature ¹³C and ²⁹Si CPMAS NMR¹⁰⁻¹².

Figure 1 shows the ²⁹Si and ¹³C CPMAS NMR spectra of poly(di n-hexylsilane). The ¹³C peak assignments were based on comparisons to previously published spectra^{13,14}. In addition, some assignments were confirmed by the synthesis of poly(di n-hexylsilane-1-¹³C) as part of a related study¹⁵. At 240°K, the ²⁹Si spectrum consists of a single peak. Between 304 and 310°K there is a sharp transition above which only a single high field peak is observed. It is assumed that at low temperatures the silicon backbone exists predominantly in the all trans form^{7,16,17}. Above the transition temperature of ca. 307°K the probability of gauche conformations is significant. Conformational mobility of the backbone results in a time averaged resonance. This is consistent with recent empirical force field (EFF) calculations which suggest that the gauche conformer is less stable¹⁸. Figure 2 shows the all trans content of the polymer as a function of temperature. This behavior mirrors thermal analysis data⁷ and other temperature dependent spectroscopic data¹⁷. The sharp transition at 305-310°K for the final 75% of the sample is particularly striking. The gradual decrease of about 25% of the all trans fraction from 250 to 305°K is probably due to some local disorder, the molecular weight distribution, and chain end effects which are to be expected in high polymers.

The ¹³C spectrum at 290°K consists of three sharp resonances and three broad resonances. Upon heating, the broad lines become sharp and well resolved while those lines which are already sharp at room temperature become only slightly narrower. At 300°K resonance 3 is composed of a broad and a narrower peak. At 304°K the the relative intensity of the narrow resonance is larger than at 300°K. At 310°K, the temperature at which only the single high field resonance is observed in the ²⁹Si spectrum, resonance 3 consists of only the single narrow peak. Although more difficult to see because of resonance overlap, resonance 2 at ca. 29 ppm similarly appears to be composed of a broad and a narrow peak with the narrow resonance increasing in relative intensity with increasing temperature. The sharper peaks in the ¹³C spectra correlate with the presence of the high field silicon resonance and the broad resonances correspond to the trans form. Surprisingly, the linewidth of resonance 1 does not seem to change appreciably with temperature although its intensity does change. The behavior of this resonance is clarified in Figure 3 which shows the presence of two peaks at 240°K of roughly equal intensity. The ability to resolve the peaks will be described elsewhere¹⁹. These spectra suggest that the C-1 carbon exists in two equally populated conformations in the low temperature state. The broadness of the C-2 and C-3 signals below ca. 300°K and C-2 through C-5 below ca. 280°K is apparently due to a combination of motional broadening²⁰ effects and perhaps a contribution due to a distribution of chemical environments, which would be due to the effect of the two different C-1 conformations on the steric crowding and conformations of the rest of the aliphatic chain.

In summary, variable temperature ^{29}Si and ^{13}C CPMAS NMR confirm that poly(di n-hexylsilane) is in a rigid form at temperatures below 310°K . It has been suggested^{7,17} that the backbone rigidity is enforced by side chain crystallization, and recent spectroscopic studies have confirmed that the backbone is predominantly planar zig-zag below the side chain melting transition temperature. The ^{29}Si NMR confirms that the thermochromism of the UV spectrum is a result of backbone disordering above the transition temperature resulting in an increasing contribution from gauche conformations at elevated temperatures. At low temperatures the aliphatic side chains appear in a form in which the methylene adjacent to the backbone is present in two packing conformations of equal population. It is likely that these two rigid conformations exist in pairs along and/or across the silane backbone in order to permit packing of the molecules in their lowest energy form. In a similar fashion the C-2 and C-3 methylenes are also significantly crowded resulting in little motion compared to typical paraffins. As the temperature increases, the signals due to the three outermost carbons begin to narrow first because of their greater degree of freedom, followed by the remaining carbons which are constrained by the steric crowding. Thus, as the side chains begin to "melt", the outermost carbons undergo enhanced rotational motion first, followed by the carbons closer to the silicon backbone. Above the transition, the silane backbone is more disordered and highly mobile which permits the greater dynamic freedom of the sidechains. It is possible that the high temperature form is in a liquid crystalline state with significant local motion but with long range order. A detailed description of the variable temperature spectra of polysilanes containing different side chains will be presented elsewhere²¹.

ACKNOWLEDGEMENTS

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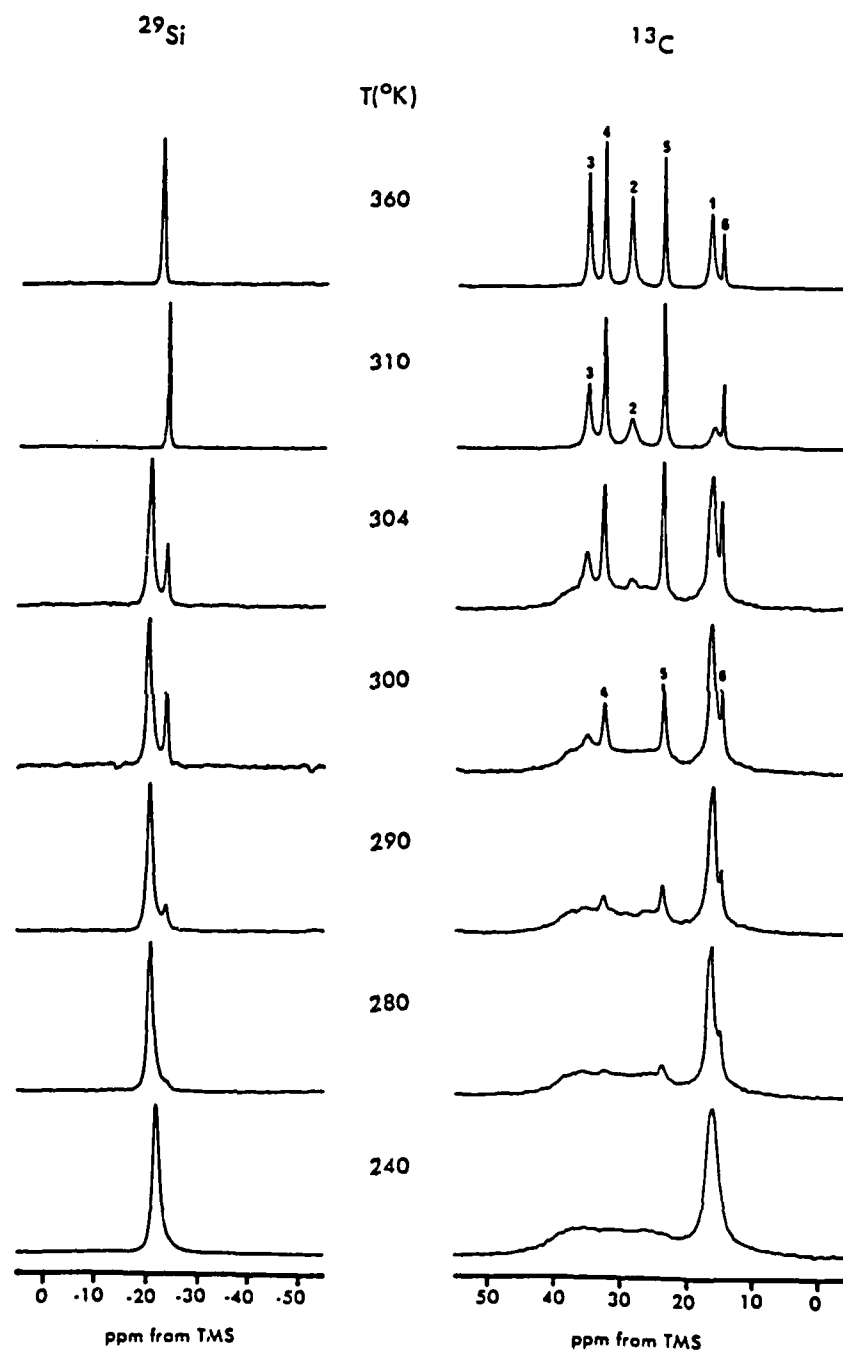


Figure 1. ^{29}Si (left) and ^{13}C (right) variable temperature magic-angle spinning spectra for poly(di n-hexylsilane) from 240 to 360°K. Silicon and carbon contact times are 10 and 3 msec., respectively, and the matching and decoupling field was ca. 57 KHz. The ^{29}Si (39.5 MHz) chemical shifts for the spectrum at 300°K are -20.8 and -24.1 ppm relative to TMS. The ^{13}C chemical shifts (50.3 MHz) at 360°K are 14.7, 16.5, 23.6, 28.6, 32.6, and 35.1 ppm relative to TMS.

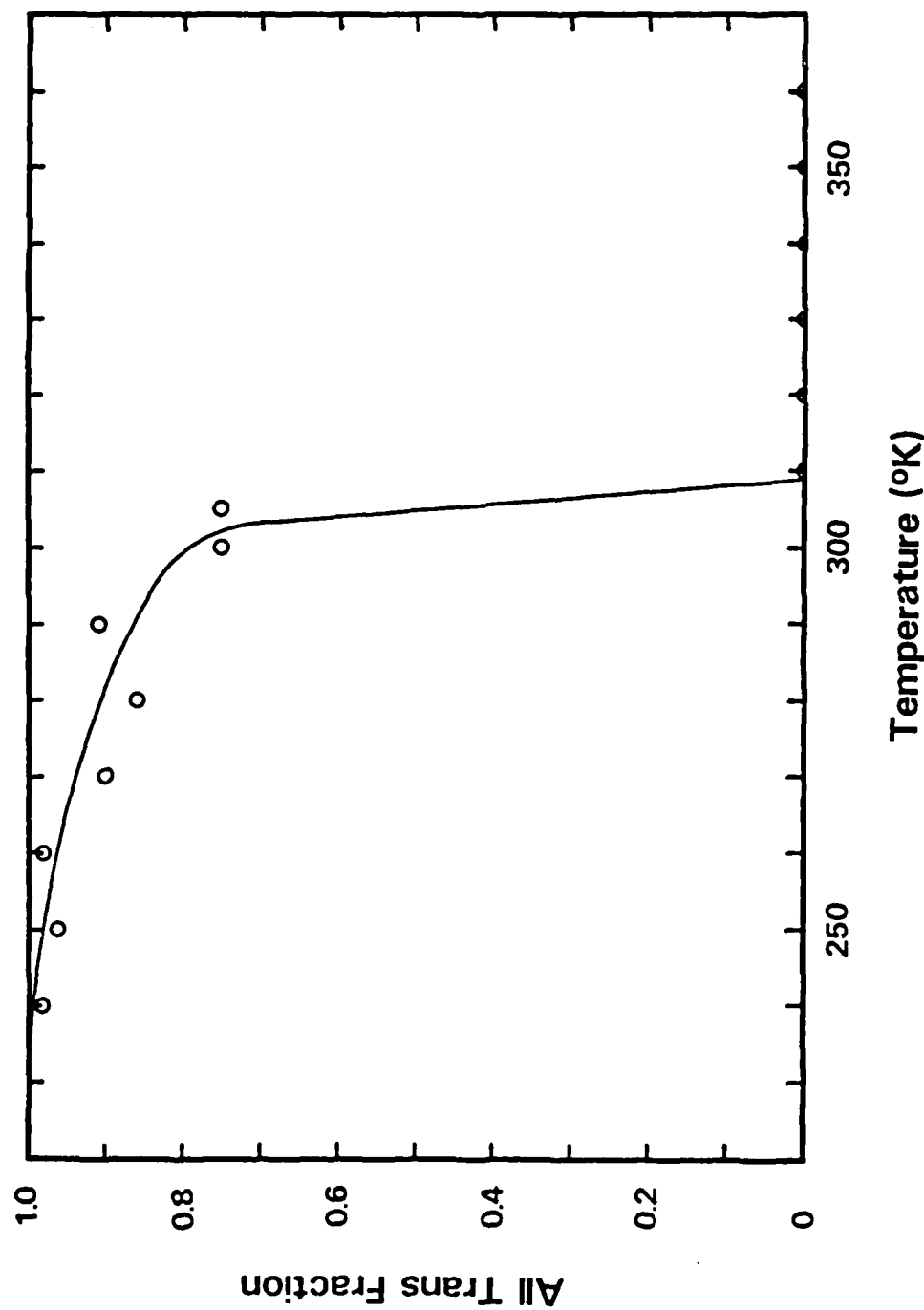


Figure 2. Normalized percentage of lowfield (all trans) component *versus* temperature as observed in the ^{29}Si NMR spectra. The data is based upon the first order assumption that the all trans fraction is equal to twice the integral of the left half of the downfield (left) peak and that the rest of the total integral is due to other components such as gauche-trans and all gauche. Although the values may not be absolutely quantitative because of different cross polarization efficiencies for the different components at different temperatures, the results are qualitatively close.

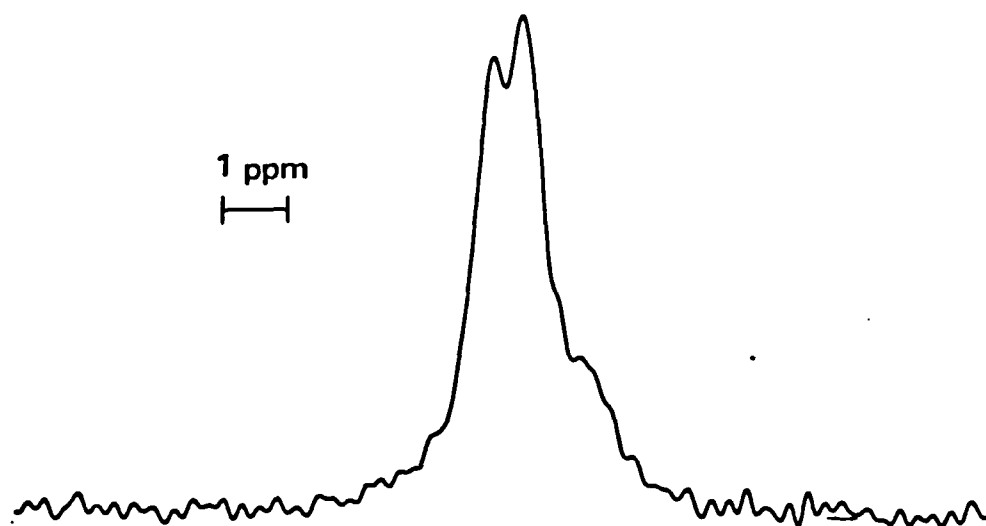


Figure 3. The C-1 region of the ^{13}C $T_{1\rho}$ CPMAS spectrum at 240°K. The cross polarization time was 2msec and the tau value during which the decoupler is off and the carbon magnetization is spin locked is 1 msec. The two peaks are of equal intensity and are spaced by 0.43 ppm. This pair of peaks was observed up to 300°K and are also of equal intensity at the other temperatures. The difference in the apparent peak heights is due to the presence of the part of the methyl resonance under the higher field peak.

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